

1030,567



# PATENT SPECIFICATION

NO DRAWINGS

1030,567

Date of Application and filing Complete Specification: April 15, 1965.

No. 16219/65.

Application made in United States of America (No. 360,402) on April 16, 1964.

Complete Specification Published: May 25, 1966.

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SEE ERRATA SLIP ATTACHED

Index at acceptance:—C3 P(10A, 10D4A, 10FX, 10P1B, 10P1C, 10P1E5, 10P1F, 10P2A2, 10P2A3, 10P2C, 10P6A, 10T1X)

Int. Cl.:—C 08 f 1/76, C 08 f 3/24

## COMPLETE SPECIFICATION

### Polytetrafluoroethylene Moulding Powder and process of its preparation

#### ERRATUM

SPECIFICATION NO. 1,030,567

Page 3, line 35, for "pot" read "plot"

THE PATENT OFFICE,  
1st March, 1968

D 101742/35

#### PATENTS ACT, 1949

SPECIFICATION NO. 1,030,567

The following amendments were allowed under Section 29 on 19th January, 1968

Page 1, line 47, page 6, line 121, for "2.15" read "2.14"

Page 3, line 9, for "2" read "3"

Page 3, line 11, for "freely" read "free"

Page 3, line 23, for "asorbition" read "adsorbition"

Page 3, line 35, delete "linen" insert "linear"

Page 3, line 60, for "minutes" read "minute"

Page 3, line 75, for "0.08" read "0.008"

Page 3, lines 84 to 91, delete "The recovered resin ..... maintained below 19°C". insert "250 Grams of the resin were added to a high speed Waring blender along with 400 ml. of distilled water at room temperature and cut for 30 seconds. This cutting was repeated four times with fresh charges of distilled water. The last charge of water was drained from the resin."

Page 5, Column I, 5th entry, for "4" read "54"

Page 5, column II, 5th entry, for "45" read "48"

Page 5, column IX, 5th entry, for "50" read "51"

Page 5, column X, 5th entry, for "45" read "55"

Page 5, column marked "Example", 8th entry, for "D<sub>50</sub>" read "D<sub>50</sub>, microns"

Page 5, column marked "Example", 9th entry, for "Tensile strength" read "Tensile strength, psi"

THE PATENT OFFICE,  
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## COMPLETE SPECIFICATION

### Polytetrafluoroethylene Moulding Powder and process of its preparation

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of polytetrafluoroethylene molding powder, and, more particularly, to the preparation of polytetrafluoroethylene powders having improved flow properties and a reduced tendency to discolor upon sintering.

Hitherto known polytetrafluoroethylene powders have exhibited poor flow properties, due to the tendency of the respective particles to intermesh. In addition, preforms made from hitherto known particulate polytetrafluoroethylene have shown a marked tendency to discolor upon sintering. This discoloration has been in the form of graying or the appearance of black spots within the moldings resulting in the disadvantage that the moldings do not present an attractive appearance. The discoloration in the sintered preform is increased when the preform is sintered in the absence of air, for example, when sintered in an inert atmosphere or while confined within a mold.

According to the present invention we provide a process for the preparation of a particulate polytetrafluoroethylene resin, which comprises polymerising tetrafluoroethylene in an aqueous medium containing a free radical initiator and from 150 to 650 ppm. of a dissolved basic ammonium compound which is free of metallic ions, said ammonium compound serving to maintain the pH of the medium at at least 7, and the concentration of dissolved metal in the medium being maintained below 50 ppm.

In general, the particulate molding powders prepared by this process will have a standard specific gravity of from 2.15 to 2.2, a specific surface area of from 1 to 9 square metres per gram (as measured by nitrogen adsorption) and a percentage reflectance of at least 60. In preferred molding powders the standard specific gravity is from 2.15 to 2.175 with a sub-sieve sizing of less than 5 microns. The crystallinity of the resin should preferably be in excess of 94 per cent.

It has been found in the course of research leading to the present invention that when tetrafluoroethylene is contacted with an aqueous medium containing a free radical initiator and less than 50 ppm liquid weight of dissolved metallic ions the resultant product obtained therefrom will have a marked tendency to resist discoloration upon sintering in the absence of air. When the concentration of metallic ions in the aqueous medium exceeds 50 ppm, the resultant powder has a far increased tendency to discolor upon sintering in the absence of air. While it has been known that a relatively inert reaction vessel such as one made of stainless steel must be used to prevent corrosion which results in impurities in the final product, it has also been found necessary to maintain the pH of the reaction medium at a level of at least 7 in order to prevent acidic attack upon the polymerization vessel. Such acidic attack results in the presence of metallic ions, thus a buffering agent must be used in order to maintain the pH of the aqueous medium at a level of at least 7 in order to prevent the formation of such metallic ions. It has now been discovered that such a buffering agent should be free of metallic ions, at least to an extent below 50 ppm. Such a pH may be maintained in accordance with the present invention by including in the polymerization medium specific amounts of a basic ammonium compound. These basic ammonium com-

pounds should preferably not possess any chain transfer activity to avoid the production of higher or lower molecular weight polymers than those desired. The use of such a polymerization medium has been found to yield a final product with a reduced tendency to discolor upon sintering in the absence of air. It has further been discovered that the amount of basic ammonium compound employed in the polymerization medium is critical, and must be between 150 to 650 ppm liquid weight of ammonium ion. Less than 150 ppm of ammonium ion will not serve as an effective buffer in the aqueous medium, and thus, acidic attack upon the polymerization vessel will result. The addition of more than 650 ppm of ammonium ion results in the formation of an unsatisfactory level of adhesions within the polymerization vessel. These adhesions are disadvantageous, not only because they require frequent cleaning of the reaction vessel, but also because they present an explosion hazard.

It has further been discovered that a non-metallic base may be satisfactorily employed as a buffer when the polymerization reaction is carried out at low pressure, e.g. 0.6—4 atmospheres in the presence of a redox-free radical initiator system such as that described in U.S. Patent No. 3,110,704.

It has further been found that the reduced tendency toward discoloration on sintering in the absence of air will result when a basic ammonium compound is employed in the polymerization medium when the polymerization reaction is carried out in the presence of a minor amount of a telogenically inert surface active agent, e.g. 100—500 ppm of ammonium perfluoro-octanoate.

Among the non-metallic ammonium compounds which have been found to be suitable for use in the polymerization of tetrafluoroethylene powders are ammonium baborate, ammonium carbonate, ammonium pentaborate, ammonium acid carbonate, ammonium tetraborate and ammonium hydroxide.

The heretofore produced polytetrafluoroethylene powders, in addition to having a marked tendency to discolor upon sintering in the absence of air, have possessed a further serious disadvantage in that because of the tendency of the individual particles to intermesh, they have not had a suitable powder flow. These powders cannot be fed evenly and uniformly into the extrusion machine and because of their low density, require high compressive loads in order to result in a flawless, dense preform which can be sintered to an article exhibiting the optimum properties of the polymer. Such particulate polymer has resulted in extrudates containing large permeable areas in addition to insufficiently bonded areas which on sintering result in weak spots, cracks and fissures,

making the sintered article completely unacceptable for commercial use.

While it has been found possible by special techniques to improve the moldability of molding powders as disclosed, for example, in British Patent Specification No. 853,338, these techniques impair the flow properties of the particulate polytetrafluoroethylene resins making them difficult, if not impossible, to process in automatic molding machines.

It has now been discovered that by the utilization of improved comminution procedures, the disadvantageous characteristics may be eliminated. While the patent to Thomas et al has taught the comminution of particulate polytetrafluoroethylene resin at a temperature range between 19°C and 327°C, it has been discovered that comminution below 19°C will result in substantially improved products.

Critically of comminution below 19°C stems from the fact that the crystal structure of the polytetrafluoroethylene shows a sharp change at about 19°C. This change is generally considered to be a first order crystalline transition. Below 19°C, the molecular conformation of the polytetrafluoroethylene is that of a zigzag arrangement which has been given a twist 180° per 13 carbon atoms. The repeat unit contains 13 CF<sub>2</sub> groups with a repeat distance of 16.9 Å. The x-ray fiber pattern of this material shows two intense upper layer lines, sixth and seventh layers while the other upper layer lines are either weak or missing. This shows that the unit cell is skewed in shape, probably triclinic. On the other hand, the few reflections found in the zero layer line shows that in the lateral direction, the molecules packed like cylindrical rods in a neat hexagonal arrangement with a nearest neighbor distance of 5.62 Å.

Above 19°C, however, the triclinic pattern changes to a new one with layer lines showing both the few streaks and sharp spots characteristic of a hexagonal unit cell. A distribution of intensity in the fibre pattern showed that the molecules retained a twisted zigzag conformation. The two intense upper layer lines are indexed as the seventh and eighth layer lines. This assignment is in contrast to the low temperature form for which the sixth and seventh layer lines are intense. This difference results with slight untwisting of the molecule in the 19°C transition from 180° twist per 13 CF<sub>2</sub> groups to a 180° twist per 15 CF<sub>2</sub> groups. It is this unwinding which causes the undesirable properties in the polymer powder when cut above 19°C.

The following examples are offered for a better understanding in producing particulate polytetrafluoroethylene resin of the present invention and are not to be construed as necessarily limiting its scope. Except as otherwise

- stated, all parts and percentages are by weight and all pressures are absolute. The physical properties of the particulate polytetrafluoroethylene resin employed in the following examples were determined as follows:
- Standard Specific Gravity (SSG) was determined by modification of ASTM D1457—62T employing a 1— $\frac{3}{8}$ " disc in place of the standard 2" disc. In this test a resin is preformed in a cylindrical mold in an unheated press at 5,000 psi, then freely sintered at 380°C in an air circulating oven and then carefully cooled. The chip is weighed in air and water and the specific gravity calculated. This value correlates with the molecular weight of the resin.
- SG<sub>2000</sub> is an SSG test as described above but in which the preform is molded at 2000 psi.
- ΔSG is a test to determine the difference between SSG and SG<sub>2000</sub>, and is taken as a measure of void content.
- Inherent polymer density (IPD) is a test employing infrared techniques on a SSG molded chip as a measure of void-free specific gravity.
- Specific surface area (SSA) was measured by nitrogen absorption technique.
- Average particle size and distribution were determined under ASTM test D1457—62T by wet sieve analysis. The powder was washed through a series of screens using trichloroethylene. Cumulative weight percent retained on each screen was obtained by weighing. The plot of the data on a cumulative basis was made on linen probability paper. The average weight particle size (D<sub>50</sub>) was interpolated from the plot at a point corresponding to 50% cumulative weight.
- Tensile strength determinations were run according to ASTM test D1457—62T.
- Reflectance, measured in percent, was determined by first preparing a preform from 10 grams of cut, washed resin using a 1" diameter cylindrical die in a press at 5,000 pounds per square inch and maintaining this pressure for two minutes. The resultant preform was placed in a close-fitting glass tube together with a control chip. Dead space in the tube was occupied by glass wool and each chip was separated from its neighbor by an aluminum foil disc. The sintering tube was attached via an adapter to a vacuum line with pressure tubing, and evacuated overnight to a pressure of 0.1 mm. The tube was then sealed under vacuum and placed in an aluminum hot block preheated to 390°C. A temperature of 380°C was maintained on the block for one hour, after which the block was allowed to cool to 300°C at 1°C/minutes and then the tube was removed to cool in air. At ambient temperature, the tube was opened to the atmosphere and the sintered chips removed. A one inch slice was then microtomed from one circular face of each chip to eliminate any surface contamination. The chips were then compared on a Color Master Differential Color Meter with an enamel plate as standard, and results were obtained as percent reflectance.
- EXAMPLE I.**
- A stainless steel polymerization vessel of 100 parts water capacity was evacuated; charged with 65 parts of deoxygenated distilled water containing a concentration of 0.08 gm. moles/l ammonium carbonate buffer and 41 ppm ammonium persulfate; heated to 67°C; pressured with tetrafluoroethylene to 175 psig. and stirred with a flat paddle agitator at an agitator speed of 600 r.p.m. Polymerization commenced shortly after the tetrafluoroethylene was added. At the conclusion of the run, 25.41 parts of polytetrafluoroethylene resin were recovered. The recovered resin was passed through a Taylor-Stiles Giant Mill, Model VFS—TS—06—SSB, operated at about 9000 r.p.m. and employing suitable cutters until the average particle size of the resin was reduced to 20 microns. During the comminution, the resin was maintained below 19°C. Drying trays were then filled to a depth of one inch (1") with the comminuted resin. The trays were placed in an oven and the resin was dried for about 16 hours at a temperature of about 120°C. The resultant particulate polytetrafluoroethylene resin was subjected to various tests and the results are summarized in Table I.
- EXAMPLE II.**
- The procedure of Example I was repeated utilizing an aqueous medium containing a concentration of 0.014 gm. moles/l of ammonium carbonate buffer and 41 ppm of ammonium persulfate. The resultant resin was subjected to various tests and the results are summarized in Table I.
- EXAMPLE III.**
- The procedure of Example I was repeated substituting a concentration of 0.014 gm moles/l borax for the ammonium carbonate. The resultant resin was subjected to various tests and the results are summarized in Table I.
- EXAMPLE IV.**
- The procedure of Example I was repeated substituting a concentration of 0.014 gm. moles/l ammonium tetraborate buffer for the ammonium carbonate. The resultant resin was subjected to various tests and the results are summarized in Table I.
- EXAMPLE V.**
- The procedure of Example I was repeated substituting a concentration of 0.014 gm. moles/l ammonium pentaborate for the ammonium carbonate. The resultant resin was subjected to various tests and the results are summarized in Table I.
- EXAMPLE VI.**
- The procedure of Example I was repeated substituting a concentration of 0.014 gm

moles/l ammonium acid carbonate buffer for the ammonium carbonate. The resultant resin was subjected to various tests and the results are summarized in Table I.

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**EXAMPLE VII.**

The procedure of Example I was repeated omitting the ammonium carbonate. The resultant resin was subjected to various tests and the results are summarized in Table I.

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**EXAMPLE VIII.**

The procedure of Example I was repeated utilizing an aqueous medium containing a concentration of 0.014 gm. moles/l of ammonium carbonate buffer, 41 ppm ammonium persulfate and 400 ppm ammonium perfluorooctanate. The resultant resin was sub-

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jected to various tests and the results are summarized in Table I.

**EXAMPLE IX**

The procedure of Example VIII was repeated substituting a concentration of 0.014 gm. moles/l borax buffer for the ammonium carbonate buffer. The resultant resin was subjected to various tests and the results are summarized in Table I.

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**EXAMPLE X**

The procedure of Example I was repeated substituting a concentration of 0.11 gm. moles/l ammonium hydroxide for the ammonium carbonate. The resultant resin was subjected to various tests and the results are summarized in Table I.

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TABLE I

Example	I	II	III	IV	V	VI	VII	VIII	IX	X
Buffer	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Borax	(NH <sub>4</sub> ) <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	(NH <sub>4</sub> ) <sub>2</sub> B <sub>6</sub> O <sub>7</sub>	NH <sub>4</sub> HCO <sub>3</sub>	None	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Borax	NH <sub>4</sub> OH
Buffer Concentration gm. moles/l.	0.008	0.014	0.014	0.014	0.014	0.014	—	0.014	0.014	0.011
SSG	2.1467	2.1430	2.1488	2.1658	2.1609	2.1457	2.1497	2.1446	2.1479	2.1474
SG <sub>2000</sub>	2.0923	2.0946	2.0937	2.1254	2.1238	2.1052	2.1109	2.1006	2.0966	2.0921
ΔSG × 10 <sup>3</sup>	44	45	55	40	37	40	39	44	50	45
IPD	2.171	2.176	2.172	2.164	2.163	2.170	2.184	2.173	2.175	2.180
SSA(m <sup>2</sup> /gm)	1.38	1.2	1.4	1.75	2.21	1.4	1.4	1.3	1.4	1.2
D <sub>90</sub>	377	412	394	443	462	420	373	407	391	395
Tensile strength	2673	2843	2495	2463	2001	2729	2370	2695	2510	2726
Elongation (%)	210	237	188	198	151	220	195	211	193	243
Reflectance	77.1	75.1	45.9	62	62.5	76.4	61.9	60	44.5	76.8
Visual	V. White	V. White	Dark Gray	Off White	Off White	V. White	Spotty White	White	White	V. White

## EXAMPLE XI.

A stainless steel polymerization vessel of 850 parts water capacity was evacuated; charged with 599 parts of deoxygenated distilled water containing per million parts, 1746 parts ammonium carbonate, 100 parts each of ammonium persulfate, ammonium bisulfite, and ammonium perfluorooctanoate, and 0.4 part copper as copper sulfate; heated to 55°C.; pressured with tetrafluoroethylene to 1.3 atmospheres and stirred at an agitator speed of 600 r.p.m. Polymerization commences shortly after the tetrafluoroethylene is added. The reaction is continued for about 3 hours, during which time stirring is continued at 600 r.p.m.; temperature is held at 55–60°C.; pressure is held at 1.3 to 1.7 atmospheres by addition of tetrafluoroethylene; after the solids content in the autoclave reaches about 25% mixture of polymer and water is intermittently withdrawn through a draw-off valve at the bottom of the autoclave; and make-up quantities of deoxygenated water containing 100 ppm each of ammonium persulfate and ammonium bisulfite are intermittently added so as to maintain the liquid level in the autoclave. It is observed that the power required to maintain stirrer speed remains substantially constant throughout the run. At the conclusion of the run, the autoclave is drained, flushed once with water, and found to be free of polymer adhesions. There is obtained after drying a total of 326 parts of fine, sandy, free-flowing granular polymer corresponding to a space time yield of 300 g./liter/per hour. The polymer so obtained readily passes a 0.25 inch mesh sieve, is of high molecular weight as determined by specific gravity measurements on a molded chip, and shows commercially acceptable powder flow properties. The reflectance was found to be 65.6%.

## EXAMPLE XII.

The procedure of Example XI was repeated substituting 5000 ppm borax for the ammonium carbonate. The properties of the resultant product were identical to those of Example X except in the case of reflectance which was found to be 37.9%.

## EXAMPLE XIII.

A stainless steel polymerization vessel of 265 parts water capacity is evacuated; charged with 186 parts of deoxygenated distilled water containing, per million parts, 50 parts ammonium persulfate, 301 parts ammonium perfluorooctanoate and 1720 parts ammonium carbonate; heated to 45°C; pressured to 250 psi and stirred with a flat paddle agitator at an agitator speed of 600 r.p.m. Polymerization commences shortly after the tetrafluoroethylene is added. The reaction is continued for 100 minutes during which time stirring is continued at 600 r.p.m. and the temperature is held at 45–50°C. There was

obtained 54 parts of fine, free-flowing granular polymer. This raw product was comminuted to an average particle size of 20 microns in a Taylor-Stiles Cutter, Model FS—TS—06—SSB, operated at about 9000 r.p.m. During the comminution, the temperature of the polymer was maintained at 10°C. The resultant fine powder had a SSG of 2.162, a bulk density of 360 g/l, a d50 wet sieve size of less than 20, a sub sieve size of 3.14, a shrinkage level of 3.2% and a reflectance of 66%. The crystallinity of the polymer as measured by infrared techniques was high both before and after comminution e.g., above 96% and above 94% respectively.

## EXAMPLE XIV

The product of Example I was comminuted to an average particle size of 20 microns in a Taylor-Stiles Cutter, Model VFS—TS—06—SSB at about 9000 r.p.m. The temperature of the resin was maintained at about 10°C. The reflectance was found to be 71.9%.

## EXAMPLE XV

The procedure of Example XIV was repeated using the product of Example III. The reflectance was found to be 54.0%.

## WHAT WE CLAIM IS:—

1. A process for the preparation of a particulate polytetrafluoroethylene resin, which comprises polymerising tetrafluoroethylene in an aqueous medium containing a free radical initiator and from 150 to 650 ppm. of a dissolved basic ammonium compound which is free of metallic ions, said ammonium compound serving to maintain the pH of the medium at at least 7, and the concentration of dissolved metal in the medium being maintained below 50 ppm.
2. A process according to claim 1 in which the tetrafluoroethylene is polymerised in the aqueous medium in the presence of a telogenically inert surface-active agent.
3. A process according to claim 2 in which the telogenically inert surface-active agent is ammonium perfluorooctanoate.
4. A process according to any of claims 1 to 3 in which the polytetrafluoroethylene so produced is subsequently comminuted at a temperature below 19°C.
5. A process according to any of claims 1 to 4 substantially as herein described in any of the Examples.
6. A particulate polytetrafluoroethylene resin prepared by the process claimed in claim 1, having a standard specific gravity of from 2.15 to 2.2, a specific surface area of from 1 to 9 square metres per gram as measured by nitrogen adsorption and a percentage reflectance of at least 60.
7. A particulate polytetrafluoroethylene resin according to claim 6 having a standard specific gravity from 2.15 to 2.175 and a sub-sieve size of less than 5 microns.
8. A particulate polytetrafluoroethylene

resin according to claim 7 having a crystallinity in excess of 94 per cent.

- 5 9. A particulate polytetrafluoroethylene resin according to any of claims 6 to 8 substantially as herein described in any of the Examples.

A. A. THORNTON & CO.,  
Chartered Patent Agents,  
Northumberland House,  
303—306, High Holborn, London, W.C.1.  
For the Applicants.

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